Infrared and Raman evidence for dimers and polymers in RbC_{60}

Michael C. Martin and Daniel Koller
Department of Physics, SUNY at Stony Brook, Stony Brook, New York 11794-3800

A. Rosenberg and C. Kendziora
Code 6650, Naval Research Laboratory, Washington, DC 20375

L. Mihaly
Department of Physics, SUNY at Stony Brook, Stony Brook, New York 11794-3800

The infrared- and Raman-active vibrational modes of C_{60} were measured in the various structural states of RbC_{60}. According to earlier studies, RbC_{60} has a fcc structure at temperatures above $\sim 100\,^\circ C$, a linear chain polymer orthorhombic structure when slowly cooled, and an as yet undetermined structure when very rapidly cooled ("quenched"). We show that the spectra obtained in the polymer state are consistent with each C_{60} molecule having bonds to two diametrically opposite neighbors. In the quenched state, we find evidence for further symmetry breaking, implying a lower symmetry structure than the polymer state. The spectroscopic data of the quenched phase are shown to be consistent with $Rb_2(C_{60})_2$, a dimerization of C_{60}.

AC_{60} was not discovered[1] until well after the other phases of alkali-metal-intercalated C_{60} were known, and it was found to undergo a number of structural and electronic phase transitions.[1–8] The existence of a phase consisting of linear polymer chains,[8] which is stable in air,[9,10] has stimulated recent interest in this material and could help in developing applications for alkali-metal-doped fullerenes.

At high temperatures ($\gtrsim 100\,^\circ C$), RbC_{60} has a fcc rocksalt structure[4] and is electrically conducting.[2,3,5,6] When slowly cooled, the specimen undergoes a first-order phase transition to an orthorhombic phase,[7] forming linear chains of C_{60} molecules along the a direction (the face-diagonal direction of the fcc phase).[8] These chains have been proposed to be $[2+2]$ cycloaddition C_{60} polymers.[11] When RbC_{60} samples are cooled extremely rapidly from the fcc phase to below $\sim 0\,^\circ C$ a metastable phase is produced.[3,6] This "quenched" phase is insulating[6] and relaxes back to the stable polymer chain phase, with a strongly temperature dependent time scale.[3,6] Dimers forming from $[2+2]$ cycloaddition or a single bond between two free radical C_{60} molecules have been suggested as a possible structure.[12] To date, x-ray scattering structural studies of this phase are still incomplete.[13] Vibrational spectroscopy, however, can help determine the symmetry of the C_{60} molecules in this quenched phase by observing which vibrational modes are infrared (ir) or Raman active.

In this paper we show that the ir and Raman vibrational spectra of the slowly cooled and quenched states are indeed consistent with polymerized and dimerized C_{60} structures, respectively. Using this C_{60} dimer picture, we are able to show that many of the characteristic properties of this phase are understood.

The C_{60} films used for the present study were evaporated and doped in vacuum-sealed Pyrex sample chambers described in detail previously.[14] Si substrates were utilized for the ir measurements, and MgO substrates were used for the Raman measurements. During doping, ir spectra obtained *in situ* were used to monitor the stoichiometry of all samples by measuring the position of the $F_{1u}(4)$ vibrational mode.[15,16] Once $Rb_x C_{60}$ samples with the majority phase $x = 1$ were produced, the alkali-metal appendages were removed from the Pyrex chambers, leaving permanently sealed chambers of essentially known stoichiometry. These rugged, portable chambers allowed a number of measurements under a variety of thermal conditions. A copper block with a heater resistor and thermocouple was attached to each chamber in order to regulate and measure the sample temperature by means of a temperature controller. Quenching was accomplished by pouring liquid nitrogen directly on the sample chambers. Typically, the sample temperature dropped from $125\,^\circ C$ to $-200\,^\circ C$ in approximately 30 s.

ir spectra were obtained at 2 cm^{-1} resolution on a Bomem MB-155 Fourier transform spectrometer and referenced to spectra of the empty sample chamber at the same temperature. Raman spectroscopy was performed using the 514.5 nm Ar$^+$ laser line and a Dilor XY triple monochromator with a charge-coupled-device (CCD) detector at a resolution of ~ 5 cm^{-1}; care was taken to use low laser powers and to monitor the $A_g(2)$ mode when the sample was in a temperature range where photoinduced effects (photopolymerization or photoexcitation) of C_{60} have been observed[17] [the Raman-active $A_g(2)$ mode shifts when C_{60} becomes photopolymerized or photoexcited].

The ir transmission spectra obtained for all structures are presented in Fig. 1. The fcc data (lowest curve) reveal only the four F_{1u}-derived vibrational modes, as labeled. The $F_{1u}(4)$ mode shows small amounts of pure C_{60} and $Rb_6 C_{60}$, labeled $x = 0$ and $x = 6$, respectively, in the mostly RbC_{60} sample [the $F_{1u}(4)$ absorption of the $x = 6$ compound appears large in Fig. 1 only because
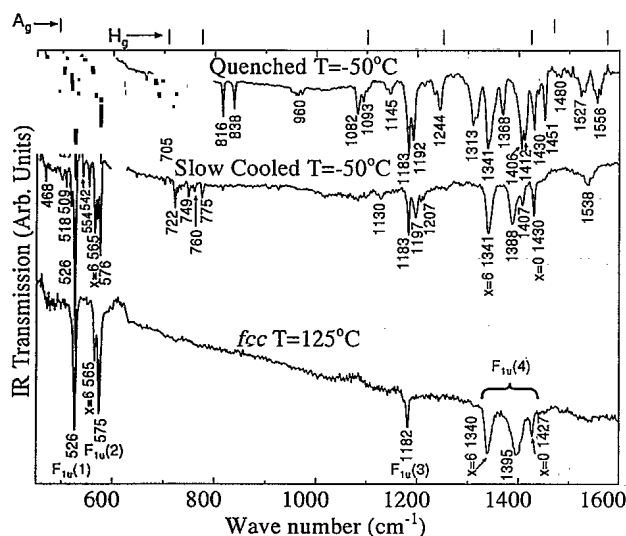
FIG. 1. Infrared transmission spectra of a RbC$_{60}$ sample at several temperatures in the energy range covering nearly all C$_{60}$ vibrational modes. The bottom curve is the spectrum of the fcc (high temperature) phase of the sample. The middle curve was obtained by slowly cooling the sample from its fcc state to the polymer state. The top spectrum was measured after the sample was rapidly cooled from high temperature to the "quenched" state. Backgrounds have been subtracted and the three spectra have been scaled to aid visual comparison. The center position of each observed mode is annotated beneath the respective spectral line. Small vertical lines above the figure indicate the positions of the Raman-active A_g and H_g vibrations of pure C$_{60}$.

FIG. 2. Raman spectra of a RbC$_{60}$ sample in its fcc structure (bottom panel), its polymer state (middle), and its "quenched" state (top). The respective temperatures are indicated on the curves. The ten Raman-active modes of pure C$_{60}$ are labeled in the bottom panel; the frequencies of newly activated modes are labeled for the quenched and polymer state spectra in the upper two panels. Inset sketches represent the dimer and polymer structures of the C$_{60}$ molecules in the quenched and slow-cooled states of RbC$_{60}$, respectively.

the mode in the $x = 6$ material is much stronger than in other stoichiometries[15,16]. The approximate center positions (in cm^{-1}) of all observed absorptions of the slow-cooled (middle curve) and quenched (top curve) states are labeled in the figure. Note that the overall transmission of the quenched phase is very different from those of the fcc and polymerized phases (the fcc and polymerized phases are electrically conducting and have low transmissions, while the quenched phase is insulating and has a high transmission[6]). For easier comparison, the ir spectra have been scaled such that the vibrational absorptions due to small amounts of other stoichiometric phases (labeled $x = 0$ and $x = 6$ in Fig. 1) appear approximately equal in magnitude. Since the strengths of these "impurity" modes should be independent of the state of the predominant RbC$_{60}$ in any given sample, this scaling allows meaningful visual comparisons of the modes seen in each phase.

We present the Raman spectra for all three states in Fig. 2. The bottom panel shows the fcc phase spectrum with the ten known Raman vibrational modes of C$_{60}$ labeled; these appear unchanged from the pure C$_{60}$ vibrations (while the sample is known to be majority $x = 1$ phased by ir spectroscopy, this Raman spectrum is probably dominated by a surface layer of the $x = 0$ "impurity" phase). The middle panel displays the spectrum of the polymerized state, with modes that are not seen
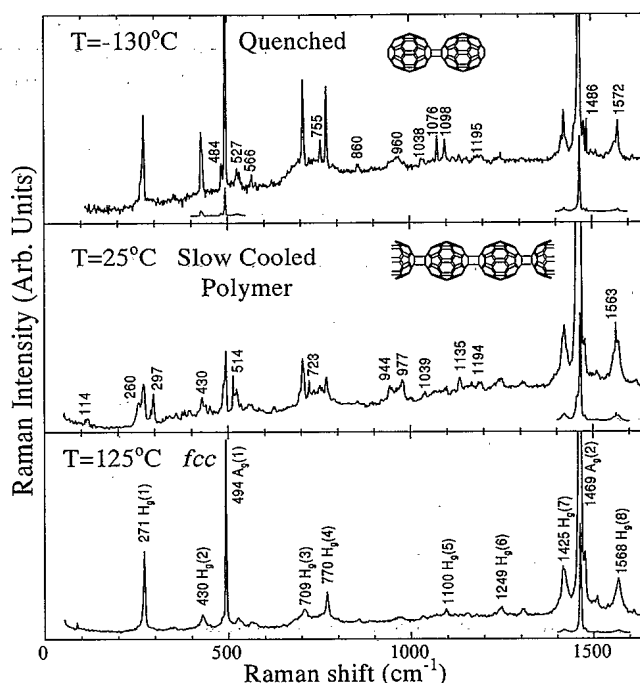
in the fcc state labeled. Inset to this panel is a drawing of the fullerenes in their polymer structure (the full orthorhombic RbC$_{60}$ structure is shown in Ref. 8). The top panel displays the spectrum of the quenched phase, with one of the proposed fullerene dimers (the $[2 + 2]$ cycloaddition possibility) shown in the inset.

We begin the discussion with the polymer chain structured state (drawn in the inset to the middle panel of Fig. 2). A drastic change in molecular environment occurs when the samples go through the first-order phase transition from the high temperature rocksalt structure, where the C$_{60}$ molecules are only bound by Van der Waals forces, to the polymer state where hexagon-hexagon (6-6) bonds on the C$_{60}$ cages are broken and bonds between neighboring fullerenes are formed. This change can be phrased in group theoretical terms as a symmetry lowering from the highly symmetric I_h icosohedral C$_{60}$ structure to the much less symmetric D_{2h} group of the polymer. Since the center of inversion site symmetry is preserved, the Raman and ir measurements remain strictly complementary. Applying the D_{2h} site symmetry to the fullerene molecule, one expects all the ungerade (antisymmetric) vibrations to become ir active and similarly all the gerade (symmetric) modes to become Raman active. Thus, the number of ir- and Raman-active modes will be greatly increased over fullerene compounds with no C$_{60}$-C$_{60}$ bonds (such as the fcc phase of RbC$_{60}$).

In agreement with this prediction, the RbC_{60} polymer ir spectrum in Fig. 1 indeed reveals at least 12 absorptions, in addition to the four F_{1u}-derived modes, which must have ungerade symmetry. Analogously, the Raman spectrum of this phase (middle panel of Fig. 2) also reveals many newly Raman-active vibrations which must be gerade modes. Since the parity of these modes is determined, these results can help to sort out the symmetries of ir- and Raman-forbidden vibrational modes of pure C_{60} seen in previous measurements.[18-20]

In the polymer state, in addition to the appearance of these new modes, the $F_{1u}(3)$ mode at 1182 cm^{-1} splits into two modes at 1183 and 1197 cm^{-1}, and the $F_{1u}(4)$ mode at 1395 cm^{-1} splits into modes at 1388 and 1407 cm^{-1}. These splittings are expected since vibrational motion along the polymer chain direction is perturbed much more than motion perpendicular to the chains. The F_{1u} vibrations are threefold degenerate with motions along the translational axes (x, y, and z); polymerization breaks this degeneracy and a split mode is observed. An alternate explanation for these splittings has been offered by Pederson and Quong:[21] a mixing occurs between the z rows of the nearly degenerate $G_u(6)$ and $F_{1u}(4)$ states, creating a perturbed ir-active mode, and similarly the $F_{1u}(3)$ state mixes with the $F_{2u}(4)$ and $H_u(5)$ modes of their theoretical model. Either explanation is consistent with both the existence of the polymer state and the spectroscopic data.

Turning to the ir and Raman spectra of the quenched phase (top curves of Fig. 1 and Fig. 2, respectively), we note a number of differences relative to the polymer phase. First, many more vibrational absorptions are seen to have become ir active (at least 25 in addition to the four F_{1u}-derived modes, as compared to 12 new modes in the polymer state). Similarly, the Raman spectrum of this quenched state shows several more vibrational modes than are observed in the polymer state. Second, the $F_{1u}(3)$ and $F_{1u}(4)$ vibrational modes are again observed to split, but by less than in the polymer case: the splittings are 9 cm^{-1} for the $F_{1u}(3)$ line and 6 cm^{-1} for the $F_{1u}(4)$ line in the quenched phase, compared to the polymer state splittings of 14 and 19 cm^{-1}, respectively. These observations indicate that a different type of symmetry breaking is occurring.

We compare our data to modes expected in the proposed quenched state structure[12] composed of C_{60} dimers, $Rb_2(C_{60})_2$. A simple sketch of two fullerene molecules in such a dimerized state is shown in the inset to the top panel of Fig. 2. The exact type of bond between the two C_{60} balls will have to be determined by further structural measurements. The sketch in Fig. 2 shows a [2 + 2] cycloaddition bond similar to the polymer state bonds, but a single bond or other bond types are equally possible and do not change the present results. This dimerized state has even lower site symmetry than the polymer state: the center of inversion is no longer at the center of a C_{60} molecule. Group theory then predicts that all gerade and ungerade vibrations will be both ir

and Raman active in the quenched state.

To test this prediction, above Fig. 1 we have placed vertical lines at the positions of the Raman-active A_g and H_g modes of pure C_{60} which fall within our measurement range. Previous measurements have shown that most vibrational modes of C_{60} soften upon doping with alkali metals.[22,15,23,16] We indeed observe modes in the ir spectra of the quenched phase that are not ir active in the polymer phase at energies just below the ideal A_g and H_g energies, in agreement with Raman studies of AC_{60} (Ref. 22) (although it is unclear which state of RbC_{60} was measured in that study). Likewise, F_{1u} modes appear in the Raman spectrum of the quenched phase (top curve of Fig. 2 at 527 and 566 cm^{-1}) but not in the polymer state Raman spectrum. These observations strongly suggest that the center of inversion symmetry is broken in the quenched state, in agreement with the dimerization picture. This allows us to assign all modes observed in the ir spectra of the quenched state that are not also in the polymer state as being derived from gerade symmetry C_{60} modes. Likewise, the modes in the Raman spectra which are seen in the quenched phase and not in the polymer phase have ungerade symmetry.

The dimer picture is in qualitative agreement with the smaller observed splittings of the $F_{1u}(3)$ and $F_{1u}(4)$ modes. Since each fullerene is altered only on one side when dimerized, as opposed to two sides when polymerized, the perturbation to the C_{60} eigenmodes will be smaller. The insulating nature of this quenched state can also be understood to be due to dimerization. The lowest unoccupied molecular orbital (LUMO) in the uncharged dimer is derived from a splitting of the triply degenerate t_{1u} electronic orbital of pure C_{60} into a singly degenerate lowest unoccupied orbital and higher energy orbitals. The two electrons donated by the two Rb atoms per dimer fill this lowest orbital and a true band insulator is formed. In this state the magnetic susceptibility is small, as observed by Jànossy et al.[3] Breaking the dimer apart (e.g., by warming) results in a partially filled band, namely, the conducting RbC_{60} fcc state.

To conclude, vibrational spectroscopy on RbC_{60} has provided strong evidence for novel structures in what has already been shown to be an intriguing fullerene compound. We propose that the quenched phase is composed of $Rb_2(C_{60})_2$ dimers and have shown that this structure is consistent with the ir and Raman data. Finally, many silent modes of pure C_{60}, which become activated in either low temperature state of Rb_1C_{60}, are classified as having gerade or ungerade symmetry.

[1] J. Winter and H. Kuzmany, Solid State Commun. **84**, 935 (1992).

[2] D.M. Poirier, T.R. Ohno, G.H. Kroll, P.J. Benning, F. Stepniak, J.H. Weaver, L.P.F. Chibante, and R.E. Smalley, Phys. Rev. B **47**, 9870 (1993).

[3] A. Jànossy, O. Chauvet, S. Pekker, J.R. Cooper, and L. Forro, Phys. Rev. Lett. **71**, 1091 (1993).

[4] Q. Zhu, O. Zhou, J.E. Fischer, A.R. McGhie, W.J. Romanow, R.M. Strongin, M.A. Cichy, and A.B. Smith III, Phys. Rev. B **47**, 13 948 (1993).

[5] R. Tycko, G. Dabbagh, D.W. Murphy, Q. Zhu, and J.E. Fischer, Phys. Rev. B **48**, 9097 (1993).

[6] Michael C. Martin, Daniel Koller, Xiaoqun Du, Peter W. Stephens, and Laszlo Mihaly, Phys. Rev. B **49**, 10 818 (1994).

[7] O. Chauvet, G. Oszlànyi, L. Forro, P.W. Stephens, M. Tegze, G. Faigel, and A. Jànossy, Phys. Rev. Lett. **72**, 2721 (1994).

[8] P.W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Jànossy, S. Pekker, G. Oszlànyi, and L. Forro, Nature **370**, 636 (1994).

[9] Daniel Koller, Michael C. Martin, Peter W. Stephens, Laszlo Mihaly, Sandor Pekker, Andras Jànossy, Olivier Chauvet, and Laszlo Forro (unpublished).

[10] S. Pekker, A. Jànossy, L. Mihaly, P.W. Stephens, O. Chauvet, M. Carrard, and L. Forro, Science **265**, 1077 (1994).

[11] S. Pekker, L. Forro, L. Mihaly, and A. Jànossy, Solid State Commun. **90**, 349 (1994).

[12] S. Pekker, A. Jànossy, and G. Oszlànyi (private communication).

[13] G. Faigel, P.W. Stephens, and Q. Zhu (private communications).

[14] Daniel Koller, Michael C. Martin, Peter W. Stephens, and Laszlo Mihaly, Rev. Sci. Instrum. **65**, 760 (1994).

[15] Michael C. Martin, Daniel Koller, and Laszlo Mihaly, Phys. Rev. B **47**, 14 607 (1993); **50**, 6538 (1994).

[16] M.J. Rice and H.Y. Choi, Phys. Rev. B **45**, 10 173 (1992).

[17] A.M. Rao, P. Zhou, K.-A. Wang, G.T. Hager, J.M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P.C. Eklund, D.S. Cornett, M.A. Duncan, and I.J. Amster, Science **259**, 955 (1993); P.H.M. van Loosdrecht, P.J.M. von Bentum, and G. Meijer, Chem. Phys. Lett. **205**, 191 (1993).

[18] Michael C. Martin, Xiaoqun Du, John Kwon, and L. Mihaly, Phys. Rev. B **50**, 173 (1994).

[19] C. Coulombeau, H. Jobic, P. Bernier, C. Fabre, D. Schütz, and A. Rassat, J. Phys. Chem. **986**, 22 (1992); G. Gensterblum, J.J Pireaus, P.A. Thiry, R. Caudono, J.P. Vigneron, Ph. Lambin, A.A. Lucas, and W. Krätschmer, Phys. Rev. Lett. **67**, 2171 (1991).

[20] Z.-H. Dong, P. Zhou, J.M. Holden, P.C. Eklund, M.S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B **48**, 2862 (1993); K.-A. Wang, A.M. Rao, P.C. Eklund, M.S. Dresselhaus, and G. Dresselhaus, *ibid.* **48**, 11 375 (1993).

[21] Mark R. Pederson and Andrew A. Quong (unpublished).

[22] M.G. Mitch, S.J. Chase, and J.S. Lannin, Phys. Rev. Lett. **68**, 883 (1992); S.J. Duclos, R.C. Haddon, S. Glarum, A.F. Hebard, and K.B. Lyons, Science **254**, 1625 (1991); P. Zhou, K.-A. Wang, P.C. Eklund, G. Dresselhaus, and M.S. Dresselhaus, Phys. Rev. B **48**, 8412 (1993).

[23] T. Pichler, J. Kürti, and H. Kuzmany, Condens. Matter Commun. **1**, 21 (1993); K.-J. Fu, S.-M. Huang, W. Karny, K. Holczer, R.B. Kaner, F. Diederich, and R.L. Whetten, Phys. Rev. B **46**, 1937 (1992).